

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

**EP 0 891 954 B1**

(12)

**EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention  
of the grant of the patent:  
**14.04.2004 Bulletin 2004/16**

(51) Int Cl.7: **C04B 35/18, C04B 38/08,  
B22C 1/02**

(21) Application number: **97948913.5**

(86) International application number:  
**PCT/ES1997/000314**

(22) Date of filing: **26.12.1997**

(87) International publication number:  
**WO 1998/029353 (09.07.1998 Gazette 1998/27)**

**(54) MOLDING SAND APPROPRIATE FOR THE FABRICATION OF CORES AND MOLDS**

**ZUR HERSTELLUNG VON KERNEN UND FORMEN GEEIGNETER FORMSAND**

**SABLE DE MOULAGE POUR LA FABRICATION DE NOYAUX ET MOULES DE FONDERIE**

(84) Designated Contracting States:  
**AT BE CH DE DK FI FR GB GR IE IT LI LU MC NL  
PT SE**

(30) Priority: **27.12.1996 ES 9602752  
22.12.1997 ES 9702667**

(43) Date of publication of application:  
**20.01.1999 Bulletin 1999/03**

(73) Proprietor: **Iberia Ashland Chemical, S.A.  
48930 Las Arenas-Guecho (ES)**

(72) Inventor: **PRAT URREIZTIETA, Jaime  
E-48930 Las Arenas-Guecho (ES)**

(74) Representative: **Carpintero Lopez, Francisco  
HERRERO & ASOCIADOS, S.L.  
Alcalá, 35  
28014 Madrid (ES)**

(56) References cited:  
**WO-A-94/23865 US-A- 4 874 726  
US-A- 5 443 603**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

**EP 0 891 954 B1**

**Description****FIELD OF THE INVENTION**

5 [0001] This invention is related to the manufacture of iron casting and, specifically, it refers to a molding sand for casting, suitable for manufacturing cores and chill molds, incorporating hollow microspheres of aluminum silicate.

**BACKGROUND OF THE INVENTION**

10 [0002] The iron casting obtained by using cores manufactured with molding sand, generally have a series of defects in their shape, such that it is necessary to subject them to machining to obtain a dimensionally correct piece. These defects are produced due to the heating the core suffers due to the effect of the molten metal poured over it, provoking its expansion and hence, the appearance of fissures on its surface. The molten metal penetrates these fissures, hence forming a kind of partition wall or laminas on the surface of the piece obtained. This undesired effect is known "veining"

15 or "rat's tail".  
[0003] At present, the cores are manufactured using molding sands and gas- or heat-cured resins, or self-curing resins, together with additives destined to improve the characteristics of the piece obtained.

[0004] To prevent the formation of "veining", a series of techniques are known and used, such as:

20 - The use of iron oxide as an additive.

[0005] The iron oxides used as additives, are destined to minimize the problems created by the expansion of the silica contained in the sands, being used for such a purpose red, black, yellow iron oxides or iron oxide from Sierra Leone, which are incorporated to the mixture in percentages varying from 1 to 3%. These oxides act as a factor for the formation of feyalite, such that the "veining" is minimized during the formation of the fissure. Nevertheless, this technique besides not eliminating "veining" in some cases, has as a disadvantage that the iron oxide reduces the mechanical resistance of the core and moreover the formation of feyalite increases the tendency to penetration, causing the external surface of the piece obtained to present irregularities, which should be treated later.

30 - Use of wood flours and coal powder.

[0006] According to this technique, wood flour or coal powders are added in proportions varying from 1 to 3%. These flours burn during melting, hence leaving free gaps distributed throughout the volume of the core, permitting that the expansion of the silica is produced in these gaps without the need to increase the external size, hence avoiding the appearance of fissures provoking "veining". The main disadvantage of this technique is that when the flours burn, a large amount of gas is produced which, on circulating, may result in dimensional problems in the pieces obtained. Likewise, with this type of additive, a reduction in the mechanical resistance of the cores is produced.

40 - Use of titanium oxide as an additive

[0007] This new technique described in the US Patent Number 4.735.973, is based on the use of titanium oxide additives, the additive being present at percentages varying between 0.5 and 5% of the total amount of sand and said additive containing between 15 and 95% titanium oxide. With this technique, thermal expansion is reduced, preventing, as a result "veining", maintaining the mechanical resistance of the cores and not producing an increase in gas production. The disadvantage of this technique lies in the fact that the cores obtained possesses a certain tendency to penetration, it being necessary to apply paints or other treatments on the surface of the cores obtained before proceeding to melting the piece.

50 - Use of natural sands of low expansion

[0008] This new technique uses for the formation of the core, special sands of the rounded or sub-angular silica type, chromite sands, zirconium sands and olivine sands, which, due to their different degrees of thermal expansion, result in the reduction of "veining", and even to its total elimination. The basic disadvantage of this technique is the high cost of this type of sand, with the consequent increase in the cost to obtain the cores.

55 - Use of electrofused sands of low expansion

[0009] According to this technique, the silica sand normally used for the manufacture of cores is melted in electric

ovens, until obtaining a kind of paste without expansion capacity. Then, the paste obtained is ground until obtaining a sand powder which is mixed approximately at 50% with silica sand. In this way, the expansion of the core is avoided, since the powder obtained from the silica paste does not have a capacity for expansion and hence, neither produces fissures nor the corresponding veining. The basic disadvantage of this technique is the greater complexity of the production process, which makes the final cost to obtain the cores more expensive.

[0010] As may be appreciated, the techniques normally used to prevent the formation of "veining" consist either in the use of additives (iron oxide, titanium oxide, wood flours and coal powder) or in the use of special sands (natural sands of low expansion or electrofused sands of low expansion).

[0011] Now it has been found that it is possible to improve the quality of the iron casting by using cores or molds manufactured with molding sands incorporating hollow microspheres of aluminum silicate.

[0012] As a result, a purpose of this invention comprises a molding sand for casting which incorporates hollow microspheres of aluminum silicate.

[0013] An additional purpose of this invention comprises a process to manufacture cores or chill molds including the use of the molding sand indicated above. The resulting cores and molds also comprise a purpose of this invention.

[0014] Another additional purpose of this invention comprises a process to manufacture iron casting including the use of the cores or molds mentioned above. The resulting iron casting also comprises a purpose of this invention.

[0015] Compositions suitable for manufacturing moulds for metal castings comprising aluminium silicate microspheres are known from WO-A-94/23865.

## SUMMARY OF THE INVENTION

[0016] The invention provides a molding sand for casting which incorporates hollow microspheres of aluminum silicate in an amount between 1 and 30% by weight with respect to the total amount of molding sand.

[0017] The composition is specified in claim 1.

[0018] The molding sand, purpose of this invention, is suitable to manufacture cores and chill molds which, in turn, may be used in the manufacture of iron casting.

[0019] The use of hollow microspheres of aluminum silicate prevents the appearance of fissures during core expansion, but without increasing gas production and maintaining the mechanical properties of the core obtained. During melting of the piece, the expansion of the silica in the molding sand does not cause an increase of the core, but the expansion is absorbed by the internal spaces of the hollow microspheres, by which the appearance of fissures on the core surface is totally prevented and, as a result, "veining".

[0020] With the molding sand of the invention, cores or molds are obtained of lesser density, by which gas production is reduced, but without decreasing its mechanical resistance. Likewise, the penetration of the piece obtained is reduced, due to the fact that the hollow microspheres of aluminum silicate cover the interstitial spaces of the core producing an effect similar to that of paint, improving the surface of the piece obtained. Therefore, the quality of the resulting iron casting is improved due to the reduction of the defects caused by core expansion and gas production.

## BRIEF DESCRIPTION OF THE DRAWINGS

[0021]

Figure 1 shows a bar diagram in which the "veining" effect is seen for different techniques of core shaping, position 04 corresponding to the technique based on the use of a molding sand of the invention containing 10% by weight, of hollow microspheres of aluminum silicate.

Figure 2 shows a bar diagram in which the mechanical resistance obtained is seen according to the different techniques of core manufacture, the position 04 corresponding to the technique based on the use of a molding sand of the invention containing 10% by weight of hollow microspheres of aluminum silicate.

Figure 3 shows a bar diagram in which the density of the cores obtained is shown, according to the different manufacturing techniques.

Figure 4 shows a comparative diagram of "veining" and penetration obtained with molding sands containing hollow microspheres of aluminum silicate (invention) and molding sands containing titanium oxide according the US patent 4.735.973.

Figure 5 shows a bar diagram in which the tensile strength of cores obtained with molding sands of this invention is shown, containing different percentages of hollow microspheres of aluminum silicate, the curves corresponding

to the tensile strength at the exit of the box, after 24 hours and with a relative humidity of 100% being represented.

#### DETAILED DESCRIPTION OF THE INVENTION

**[0022]** The invention provides a molding sand for casting incorporating hollow microspheres of aluminum silicate at an amount between 1 and 30% by weight with respect to the total amount of sand, preferably between 5 and 25% and more preferably, between 10 and 20%, by weight.

**[0023]** Preliminary tests intended to prevent the formation of "veining" on the iron casting surface showed the possibility of using hollow microspheres of aluminum silicate as an additive for molding sands destined to manufacture cores and chill molds.

**[0024]** Further tests permitted the verification that good results are obtained when the hollow microspheres of aluminum silicate used have an aluminum content between 20 and 35% by weight, based on the weight of the hollow microspheres of aluminum silicate.

**[0025]** For their use in this invention, all kinds of hollow microspheres of aluminum silicate may be used, preferably those satisfying the aforementioned characteristics, such as those marketed by the PQ Corporation under the trade mark Extendspheres, and those marketed by Microfine Minerals Limited under the trade mark Metaspheres 50. In Table 1, the main characteristics of the different microspheres used in the tests carried out are indicated.

**[0026]** Contrary to that expected, it was surprising to verify that the hollow microspheres of aluminum silicate of the best quality, understanding as such those microspheres with a relatively high aluminum content, typically between 35 and 45% by weight, give worse results than when hollow microspheres of aluminum silicate of less quality are used, that is, with an aluminum content less than 35% by weight.

**[0027]** The tests performed with different hollow microspheres of aluminum silicate, incorporated at different proportions to the molding sand have shown that, surprisingly, the microspheres with a low content in aluminum (25-33%) give, in general, the best results regarding "veining" and penetration, in turn maintaining the mechanical properties of the core obtained, moreover observing that an increase in the percentage of aluminum in the microspheres does not imply an improvement in the results of said effects ("veining" and penetration), but, on occasions, the opposite occurs [see Table 5, (Example 5)].

**[0028]** Moreover, the studies performed showed that the best results regarding veining and penetration do not only depend on the aluminum content, but other factors also have an influence, such as the size of the microspheres and the thickness of their walls. Particularly, it has been observed that hollow microspheres of aluminum silicate are suitable having a wall thickness between 3 and 10% of the microsphere diameter and a particle size between 10 and 350 micrometers ( $\mu\text{m}$ ).

**[0029]** As may be seen in Table 4 (Example 4), the microspheres giving the best results are those identified as Metaspheres 50 and Extendspheres SG, since they have a crushing strength of 189.37 kg/cm<sup>2</sup> (2.700 psi) with an aluminum content between 25 and 30% by weight, a wall thickness of 5%, with respect to the particle diameter (Extendspheres SG) and from 3 to 7% with respect to the diameter of the particle (Metaspheres 50), and an average particle size of 150  $\mu\text{m}$  (Extendspheres SG) and between 10 and 250  $\mu\text{m}$  (Metaspheres 50).

**[0030]** The molding sand of the invention may also contain other conventional components, like casting aggregates, binders and other optional components used in this sector of the technique.

**[0031]** The invention also provides a process to manufacture a core or chill mold by means of a cold process comprising:

- (A) introducing the molding sand, purpose of this invention, into a mold to form a core or non-cured mold;
- (B) placing said core or non-cured mold of stage (A) into contact with a gaseous cured catalyst;
- (C) permitting said core or non-cured mold resulting from stage (B) to cure until said core or mold may be handled; and
- (D) separating said core or mold from the mold.

**[0032]** In another embodiment, the invention also provides a process to manufacture iron casting comprising:

- (A) inserting the core or mold manufactured from the molding sand, purpose of this invention, in a casting device;
- (B) pouring the metal, in a liquid state, in said casting device;
- (C) letting the metal poured into the casting device cool and solidify; and

(D) separating the molten metal piece from the casting device.

**[0033]** The following examples serve to illustrate the invention. In Table 1, the main characteristics of the hollow microspheres of aluminum silicate used in the execution of these examples are shown.

5

10

15

20

25

30

35

40

45

50

55

Table 1  
 Characteristics of different hollow microspheres of aluminum silicate

Product	Aluminum content (%)	Wall thickness	Particle size (μm)	Crushing resistance (kg/cm <sup>2</sup> )	Softening point (°C)
Extendospheres SLG	43,3	= 10% Ø	10-300	562,48	1.800
Extendospheres SL180	43,3	= 10% Ø	10-180	562,48	1.800
Extendospheres SL150	43,3	= 10% Ø	10-150	562,48	1.800
Extendospheres SG	25-30	= 10% (radio)	10-300 (media 130)	189,37	1.200-1.350
Extendospheres XEG	25-30	= 10% (radio)	10-350 (media 162)	189,37	1.200-1.350
Extendospheres XOL200	15		100 (media)	7,03	1.000
Metaspheres 50	26-33	3-7% Ø	10-250	196,8-1.968,1	1.200-1.350

Extendospheres is a trade mark of The Pg Corporation

Metaspheres is a trade mark of Microfine Minerals Ltd.

**EXAMPLE 1**Study of the use of hollow microspheres of aluminum silicate as an additive for molding sands

**[0034]** To assess the possible use of hollow microspheres of aluminum silicate as an additive for molding sands, destined to manufacture casting cores, on the one hand some cores were formed using different resins and conventional additives, and on the other hand, other cores from a molding sand, to which hollow microspheres of aluminum silicate had been added, then studying "veining" and the tensile strength of the cores obtained. The techniques used to manufacture the different cores were conventional for each case.

**[0035]** The distinctive components for the different mixtures used to manufacture the cores, are summarized below (Table 2). In all the cases, 2% resin was used. The catalyst used in preparation 02 and 03 was SO<sub>2</sub> (gas) whilst in the remaining preparations, the catalyst used was gaseous methylethylamine (DMEA).

Table 2

Starting mixtures		
Preparation	Resin	Molding sand
01	Phenolic urethane	Silica sand (*)
02	Epoxy acrylic	Silica sand (*)
03	Acrylic	Silica sand (*)
04	Phenolic urethane	Silica sand (*) + 10% hollow microspheres of aluminum silicate (invention)
05	Phenolic urethane	Recovered furanic sand
06	Phenolic urethane	70/30 silica sand (*)/Chromite
07	Phenolic urethane	50/50 silica sand (*)/Chromite
08	Phenolic urethane	Silica sand (*) + 2% BR-022
09	Phenolic urethane	Silica sand (*) + 2% coal
10	Phenolic urethane	séggar clay
11	Phenolic urethane	50/50 electrofused silica
12	Phenolic urethane	treated olivine
13	Phenolic urethane	Thermally recovered sand
14	Phenolic urethane	Silica sand (*) + 10% Veinseal 14000

(\*): Silica sand AFA=50 rounded type, %Si>97%

**[0036]** Once the piece was prepared, the results were studied giving the value "10" to the maximum value of "veining" and a value "0" to the minimum value of "veining". Besides "veining", tensile strength was evaluated.

**[0037]** In Figures 1 and 2, bar diagrams are shown indicating the "veining" effect and tensile strength of the cores obtained. In the position 04, the properties obtained with the core obtained from molding sand containing microspheres of aluminum silicate at a percentage of 10% are shown, it being possible to observe the total absence of the "veining" effect and some good tensile strength properties.

**EXAMPLE 2**Density of different cores

**[0038]** The density of different cores obtained according to different manufacturing techniques has been determined including, for comparative purposes, a core manufactured from a molding sand containing hollow microspheres of aluminum silicate, purpose of this invention. The cores, whose density has been evaluated were prepared using the sands and additives listed below:

[1]: Additives of titanium oxide [US 4.735.973] (Veinseal).

[2]: Hollow microspheres of aluminum silicate (Invention).

- [3]: Rounded silica.  
 [4]: Sub-angular silica.  
 [5]: 70/30 Rounded silica/chromite.  
 [6]: 90/10 Silica/Additive of titanium oxide [US 4.735.973] (Veinseal).  
 [7]: 90/10 Silica/Hollow microspheres of aluminum silicate (Invention).

[0039] The results obtained are shown in Figure 3, where it may be appreciated that the cores manufactured from molding sands containing hollow microspheres of aluminum silicate, have a very reduced density with respect to that of the other cores, a density permitting the reduction of gas production and penetration in the piece obtained.

### EXAMPLE 3

#### Comparative example

[0040] Some cores were prepared as from some molding sands containing different amounts (0, 5%, 10% y 20%) of an additive selected between:

(i) hollow microspheres of aluminum silicate, and

(ii) additives of titanium oxide according to the North American Patent US 4.735.973 (Veinseal), and the effect of the same, both on "veining" and penetration has been evaluated.

[0041] The cores were prepared by mixing the sand (C-55) with 0.5%, 10% or 20% by weight of the additive in question and to the resulting mixtures, the suitable resins were added, formed and cured.

[0042] Once the different pieces were prepared, the results were evaluated, giving the value "10" to the maximum level of "veining" and penetration and the value "0" to the minimum level of "veining" and penetration. To determine the penetration of the metal in the mold, the test "Penetration 2 x 2 test casting" [AFS Transactions] was used, in which the cavities of the core in the test mold were visually examined for the existence of metal penetration.

[0043] The results obtained are shown in Figure 4, where it is clearly seen that the "veining" in both techniques is very similar and is gradually reduced until it disappears when the percentage of additive gradually increases until reaching 10%. However, the penetration using additives of titanium oxide increases as the percentage of additive increases, whilst when using hollow microspheres of aluminum silicate as an additive, the penetration remains constant and at a very reduced level.

### EXAMPLE 4

#### Preparation of cores using hollow microspheres of aluminum silicate as an additive

[0044] Some cores were prepared (crushing trials) consisting of molding sand, to which different amounts (0.5%, 10% and 20%) of hollow microspheres of aluminum silicate had been added, and the incidence thereof on the tensile strength of the cores obtained was evaluated.

[0045] The test pieces were prepared by mixing the sand (C-55) with 0.5%, 10% or 20% by weight of some hollow microspheres of aluminum silicate and to the resulting mixture, the appropriate resin mixture was added. With the mixture obtained, the crushing trials were prepared which were cured with the suitable gas.

[0046] The results obtained are collected in Figure 5, where the tensile strength of the cores obtained with different percentages of the additive, purpose of the invention, are shown, representing the curves corresponding to the tensile strength at the exit of the box, after 24 hours and with a relative humidity of 100%.

[0047] By means of a process similar to the above, some cores were prepared as from the molding sands indicated in Table 3, obtained by mixing the sand (C-55) with 0.5%, 10% or 20% by weight of hollow microspheres of aluminum silicate. In all cases, 1% Isocure® 325 (Ashland) resin and 1% Isocure® 625 (Ashland) resin, and DMEA as a catalyst were used.

Table 3

Molding sands		
Composition	C-55 sand (% by weight)	Additive (% by weight)
I	100	0



Table 3 (continued)

Molding sands		
Composition	C-55 sand (% by weight)	Additive (% by weight)
II	95	5
III	90	10
IV	80	20

[0048] The cores obtained were submitted to some abrasion resistance tests (Scratch Hardness, SH) and tensile strength tests (Tensile Hardness, TS). The results obtained are shown in Table 4.

Table 4

Mechanical resistances								
Resistance	I		II		III		IV	
composition	TS	SH	TS	SH	TS	SH	TS	SH
2 cc. 302	68	94	56	93	54	92	44	90
1 hour	76	95	72	94	74	96	60	92
24 hours	88	98	95	97	98	97	85	96
1 h. Air and 24 h. 100% humidity	23	73	35	86	30	79	26	74
Test piece weight	448,9		425,0		385,8		318,8	

[0049] The following examples were made with the purpose of selecting the most suitable hollow microspheres of aluminum silicate for their use as an additive in molding sands.

#### EXAMPLE 5

##### Evaluation of different hollow microspheres of aluminum silicate as an "anti-veining" additive

[0050] To evaluate the "anti-veining" behavior of different types of microspheres of aluminum silicate, some test pieces for crushing tests were prepared, consisting of molding sand to which different amounts of the microspheres to be evaluated had been added.

[0051] The test pieces were prepared by mixing the sand (C-55) with 10% or 20% by weight of the microspheres and to the resulting mixture 0.75% Isocure® 325 (Ashland) and 0.75% Isocure® 625 (Ashland) were added. With the mixture obtained, some test pieces for crushing were made, gassing them with Isocure® 720 (Ashland). Afterwards, they were placed in a mold for their melting with gray iron at 1,420°C.

[0052] Once the piece had been cooled, the results were evaluated, giving the value "10" to the maximum level of "veining" and penetration and the value "0" to the minimum level of "veining" and penetration. To determine the penetration of the metal in the mold, the test "Penetration 2 x 2 test casting" [AFS Transactions] was used, in which the cavities of the core were examined in the test mold to visually examined the existence of metal penetration.

[0053] The results obtained are shown in Table 5, where it may be appreciated that the best results regarding "veining" and penetration (that is, those in which "veining" and penetration was obtained with a value of zero or very near to zero) were obtained when using 20% by weight of the hollow microspheres of aluminum silicate with an aluminum content between 25 and 33% (Extendospheres SG and Metaspheres SLG, SL180 and SL150, with an aluminum content near to 45% by weight) which gave the worse results in general.

Table 5  
Study of "anti-veining" products  
Test pieces for crushing

Test piece No.	C-55 sand	Test piece weight (g)	Isocure® 325/ Isocure® 625 (1.5% resin total)							Veining	Penetration
			SL 180	SL 150	SLG	Meta. 50	XEG	SG	XOL 200		
Control A	100	175,8	--	--	--	--	--	--	--	8	2
1	90	151,5	10	--	--	--	--	--	--	9	2
2	80	122,2	20	--	--	--	--	--	--	9	2
3	90	150,1	--	10	--	--	--	--	--	9	2
4	80	124,3	--	20	--	--	--	--	--	9	4
5	90	147,2	--	--	10	--	--	--	--	9	1
6	80	121,0	--	--	20	--	--	--	--	10	0
7	90	150,0	--	--	--	10	--	--	--	4	3
8	80	123,2	--	--	--	20	--	--	--	0	0
9	90	144,6	--	--	--	--	10	--	--	2	2
10	80	117,0	--	--	--	--	20	--	--	0	1
11	90	147,0	--	--	--	--	--	10	--	2	0
12	80	122,0	--	--	--	--	--	20	--	0	0
13	90	175,4	--	--	--	--	--	--	10	9	2
14	95	176,0	--	--	--	--	--	--	5	10	5

[SL 180, SL150, SLG, XEG, SG and XOL200 are different types of Extendspheres; Meta. 50: Metaspheeres 5°; (Table 1)]

**EXAMPLE 6**Evaluation of the mechanical resistance of "anti-veining" additives

5   **[0054]** To evaluate the mechanical resistance of different types of microspheres of aluminum silicate, some tensile strength test pieces were prepared, consisting of sand to which different amounts of the microspheres to be evaluated had been added.

10   **[0055]** The test pieces were prepared by mixing the sand (C-55) with 10% or 20% by weight of the microspheres and to the resulting mixture, 0.75% Isocure® 325 (Ashland) and 0.75% Isocure® 625 (Ashland) were added. The catalyst used was DMEA. With the mixture obtained, some tensile strength test pieces were made, which were subjected to abrasion resistance (SH) and tensile strength (TH) tests. The result obtained are shown in Table 6, where it is observed that in spite of the good results obtained in the "veining" and penetration effects, also satisfactory mechanical resistances were obtained, for the cores prepared from the molding sands of the invention.

15

20

25

30

35

40

45

50

55

Table 6  
Study of the mechanical resistances of agglomerated products (sand/microspheres)

Resin Amount Catalyst	ISOCURE® 1.5 DMEA	ISOCURE® 625	ISOCURE® 325	ISOCURE® 1.5 DMEA	ISOCURE® 625	ISOCURE® 325	ISOCURE® 1.5 DMEA	ISOCURE® 625	ISOCURE® 325	ISOCURE® 1.5 DMEA	ISOCURE® 625	ISOCURE® 325
Product	100% C-55 (Control)	TS	SH	90% C-55 10% EX XEG	TS	SH	80% C-55 20% EX XEG	TS	SH	90% C-55 10% EX SG	TS	SH
Agglomerate	50 92 73 96 83 97	67 92 72 94 78 94	61 89	63 90 58 91 63 92	63 92 70 93 86 95	63 92 70 93 86 95	57 91 59 93 73 95	57 91 59 93 73 95	60 90	57 91 59 93 73 95	57 91 59 93 73 95	49 83
3 cc. 3' 1 hour 24 hours 1h air & 24 h 100% humidity	228.3	186.0	153.3	153.3	192.3	192.3	156.0	156.0	156.0	156.0	156.0	156.0
Density	6 hours of life in bank											
3 test pieces	6 hours of life in bank											
3cc. 3' 1 hour 24 hours 1h air & 24 h 100% humidity	TS	SH	TS	SH	TS	SH	TS	SH	TS	SH	TS	SH
	38 83 46 91 55 94 48 92	40 81 44 83 48 86 38 81	25 43 26 44 30 47 23 40	25 43 26 44 30 47 23 40	38 80 40 82 48 85 44 81	38 80 40 82 48 85 44 81	22 49 25 49 29 50 20 40	22 49 25 49 29 50 20 40	15 32 12 31 13 40 11 32	15 32 12 31 13 40 11 32	15 32 12 31 13 40 11 32	15 32 12 31 13 40 11 32

[MS: Metaspheres; EX: Extendspheres; TS: tensile strength; SH: abrasion resistance]

**EXAMPLE 7**Evaluation of mechanical resistances of different hollow microspheres of aluminum silicate

- 5    **[0056]** To evaluate the mechanical resistance of different hollow microspheres of aluminum silicate at 100%, some tensile strength test pieces were prepared, by mixing the microspheres (100%) to be evaluated with 3% Isocure® 323 (Ashland) and 3% Isocure® 623 (Ashland). With the mixtures obtained, some tensile strength test pieces were made which were gassed with Isocure® 702 (Ashland). The test pieces obtained were submitted to abrasion resistance (SH) and tensile strength (TH) tests. The result obtained are shown in Table 7, where it may be appreciated that the best results were obtained with Extendspheres XEG microspheres, having an average particle size (162  $\mu\text{m}$ ) greater than the Extendspheres SG microspheres (130  $\mu\text{m}$ ).
- 10

15

20

25

30

35

40

45

50

55

Table 7  
Study of mechanical resistances of different additives (with Isocure) used in the  
manufacture of sleeves

Microsphere Resin	EX SL180	EX SL150	EX SLG	METASPHERES	EX SG	EX XEG
	ISOCURE	ISOCURE	ISOCURE	50	ISOCURE	ISOCURE
Resin amount	323/623	323/623	323/623	ISOCURE	323/623	323/623
Catalyst	6	6	6	323/623	6	6
	DMEA	DMEA	DMEA	6	DMEA	DMEA
	TS	TS	TS	TS	TS	TS
4 cc. 3'	SH	SH	SH	SH	SH	SH
1 hour	49	49	47	48	36	60
24 hours	80	82	78	81	71	83
1h air & 24 h	63	52	66	43	50	66
100% humidity	86	84	87	80	80	83
	70	67	90	79	72	78
	92	86			94	95
	60	43	63	38	54	63
	85	77	87	75	79	94

[Ex: Extensospheres; TS: tensile strength; SH: abrasion resistance]

## Claims

1. A composition for the manufacture of cores and chill molds which comprises a molding sand, a resin and hollow microspheres of aluminum silicate **characterized in that** said hollow microspheres are present in the composition in an amount between 1 and 30% by weight with respect to the total amount of the sand and said hollow aluminum silicate microspheres have an aluminum content between 20 and 35% by weight of the microspheres.
2. A composition according to claim 1, wherein said hollow microspheres of aluminum silicate have a wall thickness between 3 and 10% of the microsphere diameter.
3. A composition according to claim 1, wherein said hollow microspheres of aluminum silicate have a particle size between 10 and 350  $\mu\text{m}$ .
4. A composition according to claim 1, wherein said hollow microspheres of aluminum silicate are present in the composition in an amount between 5 and 25% by weight with respect to the total amount of the sand.
5. A composition according to claim 4, wherein said hollow microspheres of aluminum silicate are present in the composition in an amount between 10 and 20% by weight with respect to the total amount of the sand.
6. Use of a composition which comprises hollow microspheres of aluminum silicate according to claims 1 to 5 for the manufacture of cores or chill molds for iron casting.
7. A process for the manufacture of a core or chill mold by means of cold process, comprising:
  - (A) introducing a composition for the manufacture of cores and chill molds according to any of claims 1 to 5, in a mold in order to form a core or non-cured mold;
  - (B) putting said non cured core or mold from step (A) in contact with a gaseous cured catalyst;
  - (C) letting said core or non-cured core or mold resulting from step (B) cure until said core or mold may be handled; and
  - (D) separating said core or mold from the mold.
8. A core or chill mold prepared according to the process of claim 7.
9. A core or chill mold for metal casting which comprise a composition including hollow microspheres of aluminium silicate according to claims 1 to 5.
10. A process to manufacture iron casting, including:
  - (A) inserting a core or chill mold, according to claim 8 and 9 in a casting device;
  - (B) pouring the metal in a liquid state, in said casting device;
  - (C) letting the metal poured into the casting device cool and solidify; and
  - (D) separating the melted metal piece from the casting device.

## Patentansprüche

1. Eine Zusammensetzung zur Herstellung von Hülse- und Kühlformen, die Formsand, ein Harz und hohle Mikrokugeln aus Aluminiumsilikat umfassen, **dadurch gekennzeichnet, dass** besagte hohle Mikrokugeln sich in der Zusammensetzung in einer Menge zwischen 1 und 30% Gewicht befinden hinsichtlich der Gesamtmenge an Sand und besagte hohle Aluminiumsilikatkugeln einen Aluminiumgehalt zwischen 20 und 35% Gewicht der Mikrokugeln haben.

2. Eine Zusammensetzung gemäss Anspruch 1, wobei besagte hohle Mikrokugeln aus Aluminiumsilikat eine Wandstärke zwischen 3 und 10% des Mikrokugeldurchmessers aufweisen.
3. Eine Zusammensetzung gemäss Anspruch 1, wobei besagte hohle Mikrokugeln aus Aluminiumsilikat eine Partikelgrösse zwischen 10 und 350 µm aufweisen.
4. Eine Zusammensetzung gemäss Anspruch 1, wobei besagte hohle Mikrokugeln aus Aluminiumsilikat in der Verbindung in einer Menge zwischen 5 und 25% Gewicht hinsichtlich der Gesamtmenge an Sand vorhanden sind.
5. Eine Zusammensetzung gemäss Anspruch 4, wobei besagte hohle Mikrokugeln aus Aluminiumsilikat in der Verbindung in einer Menge zwischen 10 und 20% Gewicht hinsichtlich der Gesamtmenge an Sand vorhanden sind.
6. Anwendung einer Zusammensetzung, die hohle Mikrokugeln aus Aluminiumsilikat gemäss Anspruch 1 bis 5 umfasst, um Hülsen- oder Kühlformen für Gussstücke herzustellen.
7. Ein Verfahren zur Herstellung von Hülsen- oder Kühlformen mittels eines Kaltprozesses, der Folgendes umfasst:
  - (A) Einführung einer Zusammensetzung für die Herstellung von Hülsen- und Kühlformen, gemäss eines der Ansprüche 1 bis 5 in eine Form, um eine Hülse oder eine ungehärtete Form zu bilden;
  - (B) Die ungehärtete Hülse oder Form des Schritts (A) in Kontakt mit dem gasförmigen gehärteten Katalysator bringen;
  - (C) Besagte Hülse oder ungehärtete Hülse, die das Ergebnis des Schritts (B) ist, aushärten lassen, bis die besagte Hülse oder Form gehandhabt werden kann; und
  - (D) Die besagte Hülse oder Form von der Form trennen.
8. Eine Hülsen- oder Kühlform hergestellt gemäss dem Verfahren des Anspruchs 7.
9. Eine Hülsen- oder Kühlform zum Metallgiessen, das eine Zusammensetzung umfasst, die hohle Mikrokugeln aus Aluminiumsilikat umfasst, gemäss den Ansprüchen 1 bis 5.
10. Ein Verfahren zur Herstellung von Eisenguss, des Folgendes umfasst:
  - (A) Einführen einer Hülsen- oder Kühlform gemäss Anspruch 8 oder 9 in eine Gussvorrichtung;
  - (B) Das Metal im flüssigen Zustand in die besagte Gussvorrichtung giessen;
  - (C) Das gegossene Metal in der Gussvorrichtung kühlen und erhärten lassen; und
  - (D) Das geschmolzene Metallteil von der Gussvorrichtung trennen.

#### Revendications

1. Une composition pour la fabrication de noyaux et de moules à coquille qui comprend du sable de moulage, une résine et des microsphères creuses en silicate d'aluminium **caractérisée en ce que** lesdites microsphères creuses sont présentes dans la composition en une quantité allant de 1 à 30% en poids par rapport à la quantité totale du sable et les dites microsphères creuses en silicates d'aluminium ont un contenu en aluminium allant de 20 à 35% en poids des microsphères.
2. Une composition selon la revendication 1, dans laquelle lesdites microsphères creuses en silicate d'aluminium ont une épaisseur de paroi allant de 3 à 10% du diamètre des microsphères.
3. Une composition selon la revendication 1, dans laquelle lesdites microsphères creuses en silicate d'aluminium ont une dimension de particule allant de 10 à 350 µm.



## EP 0 891 954 B1

4. Une composition selon la revendication 1, dans laquelle lesdites microsphères creuses en silicate d'aluminium sont présentes dans la composition en une quantité allant de 5 à 25% en poids par rapport à la quantité totale de sable.
- 5 5. Une composition selon la revendication 4, dans laquelle lesdites microsphères creuses en silicate d'aluminium sont présentes dans la composition en une quantité allant de 10 à 20% en poids par rapport à la quantité totale de sable.
- 10 6. Utilisation d'une composition qui comprend des microsphères creuses en silicate d'aluminium selon les revendications 1 à 4 pour la fabrication de noyaux ou de moules à coquille pour fonte moulée.
7. Un procédé pour la fabrication d'un noyau ou d'un moule à coquille au moyen d'un procédé à froid, consistant à:
- 15 (a) introduire une composition pour la fabrication de noyaux et de moules à coquille selon l'une quelconque des revendications 1 à 5, dans un moule pour former un noyau ou un moule non durci;
- (b) mettre le noyau ou moule non durci de l'étape (a) en contact avec un catalyseur durci gazeux;
- (c) laisser que ledit noyau ou noyau ou moule non durci provenant de l'étape (b) durcisse jusqu'à ce que ledit noyau ou moule puisse être manipulé; et
- 20 (d) séparer ledit noyau ou moule du moule.
8. Un noyau ou moule à coquille préparé selon le procédé de la revendication 7.
9. Un noyau ou moule à coquille pour fonte moulée qui comprend une composition qui inclut des microsphères creuses de silicate d'aluminium selon les revendications 1 à 5.
- 25 10. Un procédé pour la fabrication de fonte moulée qui consiste à:
- (a) insérer un noyau ou moule à coquille, selon les revendications 8 et 9 dans un dispositif de coulée;
- 30 (b) verser le métal dans un état liquide, dans ledit dispositif de coulée;
- (c) laisser que le métal versé à l'intérieur du dispositif de coulée se refroidisse et se solidifie; et
- (d) séparer la pièce de métal fondu du dispositif de coulée.

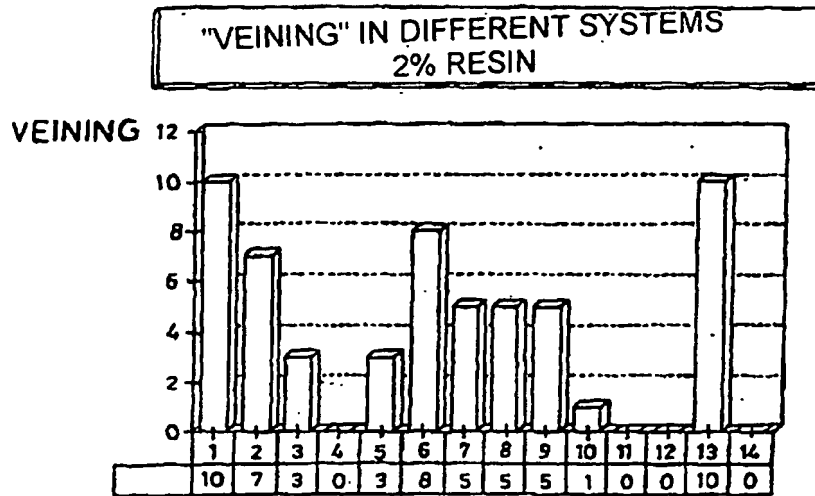
35

40

45

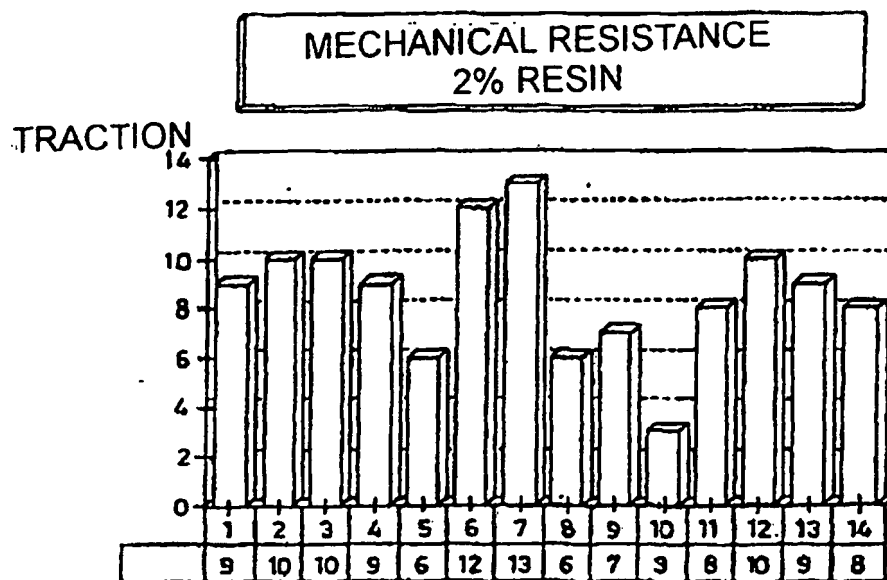
50

55



- 01.- Phenolic Urethane.
- 02.- Epoxy acrylic
- 03.- Acrylic
- 04.- Silica + 10% microsphere additive, purpose of the invention
- 05.- Furamic recovered sand
- 06.- 70/30 silica/chromite
- 07.- 50/50 silica/chromite
- 08.- Silica + 2% BR-022
- 09.- Silica + 2% coal.
- 10.- Seggar clay
- 11.- 50/50 electrofused silica
- 12.- Treated olivine
- 13.- Thermally recovered sand
- 14.- Silica + 10 Veinseal 14000

**FIG.1**



- 01.- Phenolic Urethane
- 02.- Epoxy acrylic
- 03.- Acrylic
- 04.- Silica + 10% microspheres
- 05.- Furanic recovered sand
- 06.- 70/30 silica/chromite
- 07.- 50/50 silica/chromite
- 08.- Silica + 2% BR-022
- 09.- Silica + 2% coal
- 10.- Seggar clay
- 11.- 50/50 electrofused silica
- 12.- Treated olivine
- 13.- Thermally recovered sand
- 14.- Silica + 10 Veinseal 14000

**FIG.2**

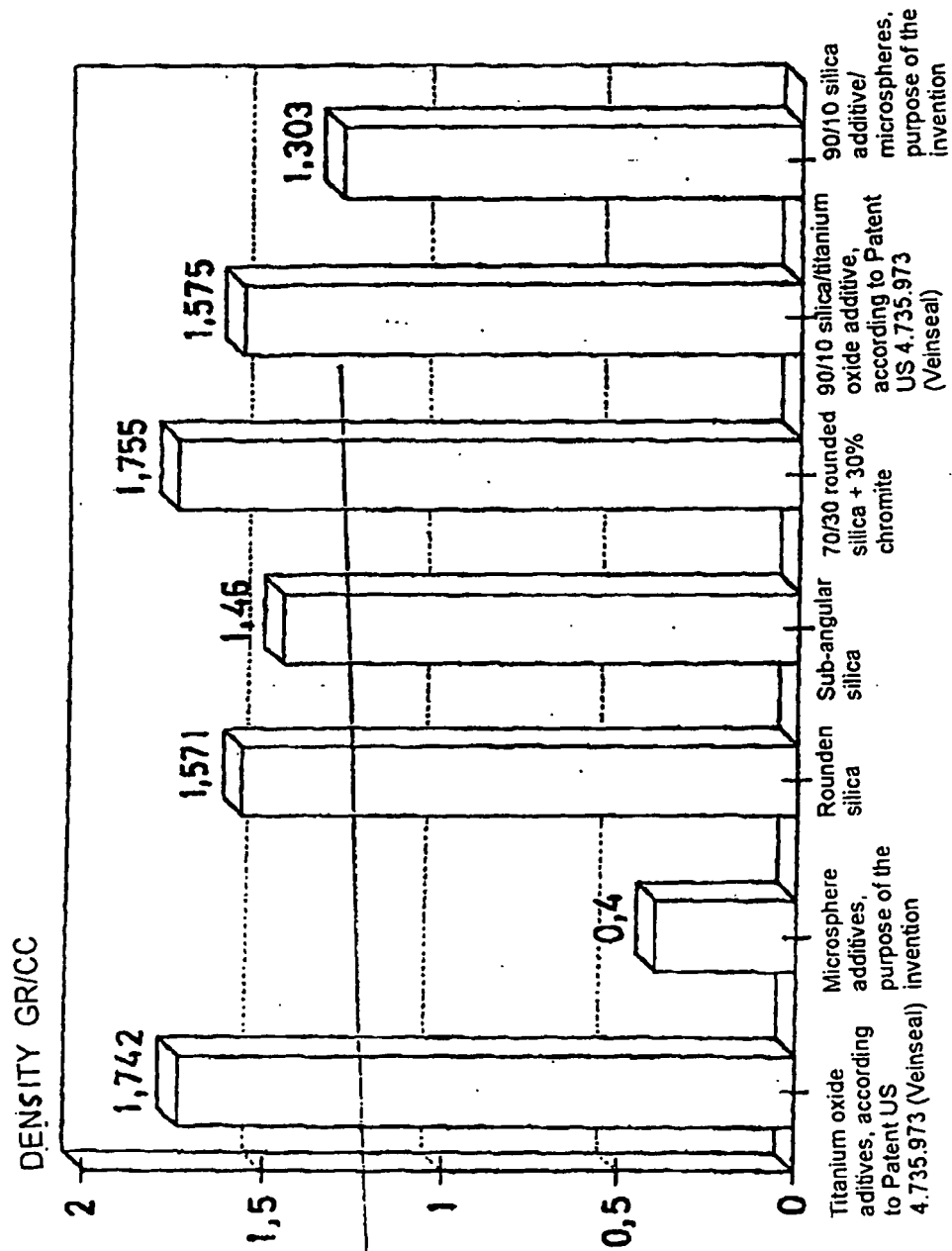
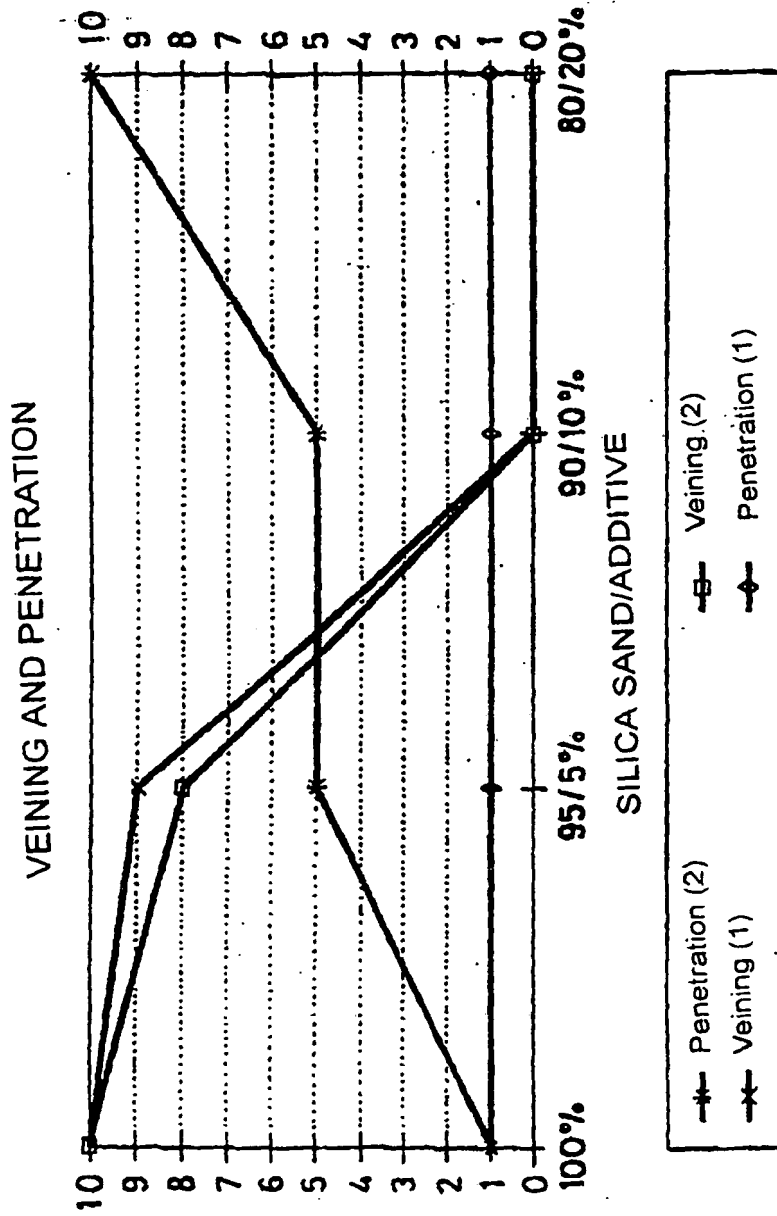


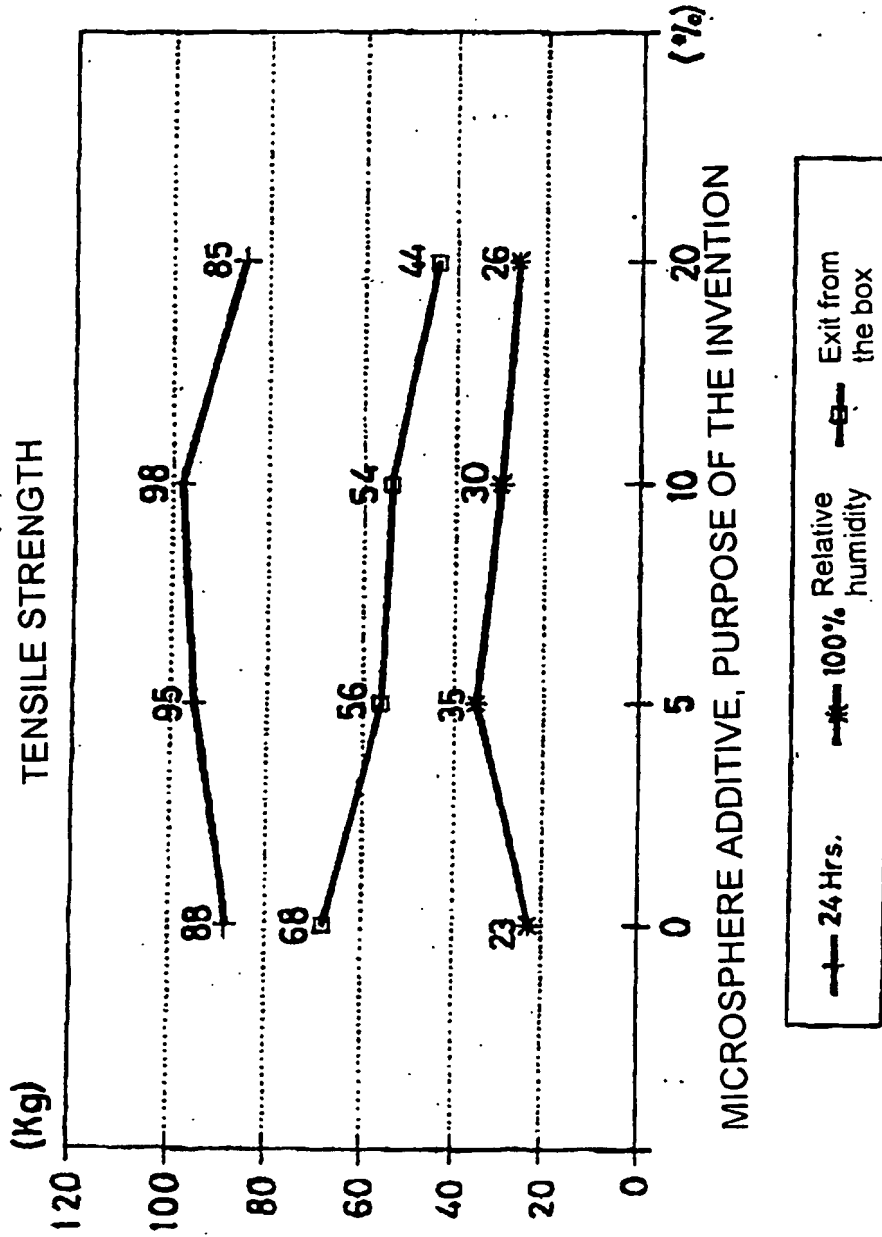
FIG.3



(1) MICROSPHERE ADDITIVE,  
PURPOSE OF THE INVENTION

(2) TITANIUM OXIDE  
ADDITIVE, ACCORDING TO  
PATENT US  
4,735,973

**FIG. 4**



**FIG.5**